UNIVERSITY OF FLORIDA

Solar Fuels from Thermochemical Cycles at Low Pressures

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Description: The project focuses on the production of solar fuels from solar thermochemical cycles employing metal/metal oxide redox pairs. These thermochemical cycles consist of a high temperature endothermic solar driven reduction step and a low temperature, slightly exothermic water or CO_2 splitting step. The high temperature step typically proceeds at temperatures above 2000 K. Hence, it poses a range of material and design challenges. According to Le Chatelier's principle, the temperature for the solar dissociation reaction decreases as the pressure inside the reactor is reduced. The central hypothesis of the project is that operating the high temperature step of metal/metal oxide solar thermochemical cycles at reduced pressures will lead to significantly relaxed temperature requirements, while the work necessary to produce the pressure difference will not significantly reduce the overall efficiency of the process.
The main goal of the project is to demonstrate the feasibility of carrying out high temperature thermal reduction of metal oxides in rarefied conditions using high intensity solar radiation from UF's solar simulator.
Budget: $100,000.00
Universities: UF
External Collaborators: Wojciech Lipinski, University of Minnesota

Progress Summary

In the reporting period progress has been made in *two areas*. Firstly, the design of *UF's high flux solar simulator* has been completed. The simulator is currently under construction. Construction is expected to be finalized in December 2010, and commissioning of the simulator is scheduled for January 2010. Secondly, a list of potentially interesting metal/metal oxide redox pairs has been compiled based on the pertinent literature. *Thermodynamic analyses* have been carried out to create a short-list of five promising metal/metal oxide pairs.

UF Solar simulator

A solar simulator system has been developed. It will provide highly concentrated radiation (approaching 5000 kW/m^2) to investigate high temperature solar thermal processes for the production of solar fuels. In particular metal/metal-oxide cycles at low pressures are of interest. The solar simulator provides highly controlled boundary conditions to the experiment.

Partially assembled solar simulator

Design and Specifications

The simulator consists of seven, 6 kW Xe-arc lamps, which closely approximate the spectral distribution of the sun. Each lamp is close coupled to an ellipsoidal mirror. All lamp/mirror assemblies focus the light onto a common focal point. The expected peak flux is 5000 kW/m^2, equivalent to a blackbody stagnation temperature of approximately 3000 K.

Redox pair selection

Based on a range of criteria including temperature requirements, toxicity, and side reactions five potentially beneficial 2-step water splitting redox cycles have been selected for experimental investigation using UF's solar simulator: Fe_3O_4/FeO, Ce_2O_3/CeO_2, ZnO/Zn, SnO/SnO_2, and In_2O_3/In_2O. Since volatile metal oxide cycles (cycles 3-5) require rapid quenching to avoid recombination, which introduces significant irreversibilities, the focus of our experimental investigations will be on the iron and cerium based cycles.

This report summarizes the activities related to the investigation of solar thermochemical processes at low pressures carried out in the PI's goup during the reporting period (December 2009 through September 2010). The main focus has been the development and construction of a high flux solar simulator. Construction is currently ongoing and first tests are planned for January 2010. Furthermore a screening of high temperature solar thermochemical fuel production cycles has been carried out. 5 cycles have been short listed. With Ce-based and Fe-based systems selected for the initial experiments.

Solar simulator

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Figure 11 The partially assembled solar simulator at UF.

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Construction

The simulator is currently under construction. Completion of the construction phase is expected in December 2010. The simulator comprises:

- An extruded, adjustable aluminum frame,
- Seven, 6 kW lamps close-coupled to elliptical mirrors to focus the radiation,
- Air cooling system to keep the lamp and mirror assembly cool,
- A power rack containing power supply equipment,
- A safety wall with a retractable door (controlled from a separate room),
- A fully controllable and customizable x-y table to mount and position experiments,
- Adequate DAQ systems as required (flux measurement, thermocouples, pressure sensors, etc.)
- Comprehensive, redundant safety systems.

Flux measurement system and Monte Carlo Simulation

In order to characterize the spatial and directional intensity distribution of concentrated radiation in the simulator's target plane, a combination of camera-based flux mapping (figure 3) and Monte Carlo ray tracing simulations will be carried out. An in-house Monte Carlo ray-tracing program [1], [2] has been employed for simulating radiative transfer in the UF solar simulator. Monte Carlo calculations will be validated using flux measurements.

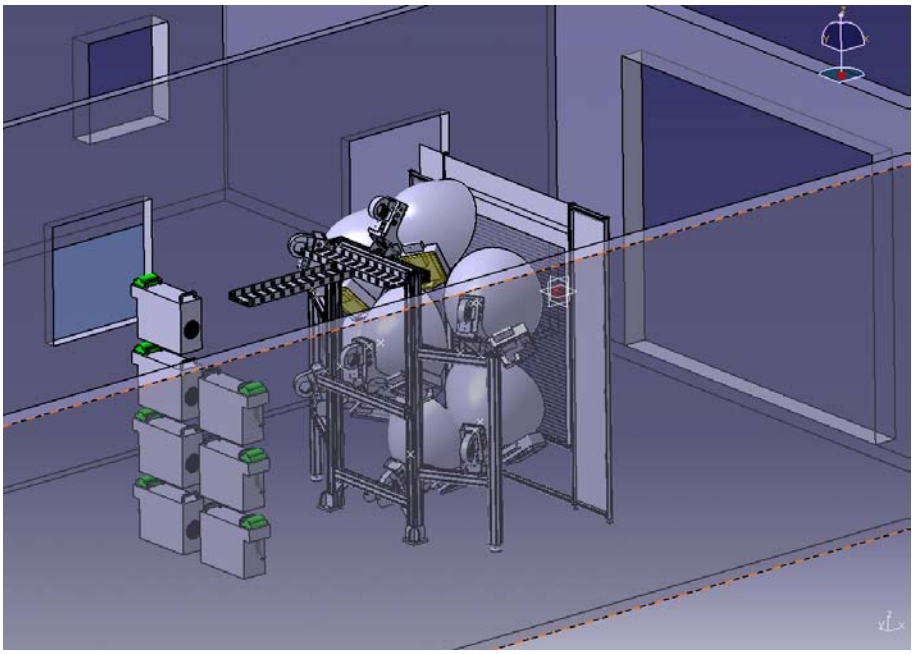

Figure 2 Three dimensional model (rear view) of the solar simulator.

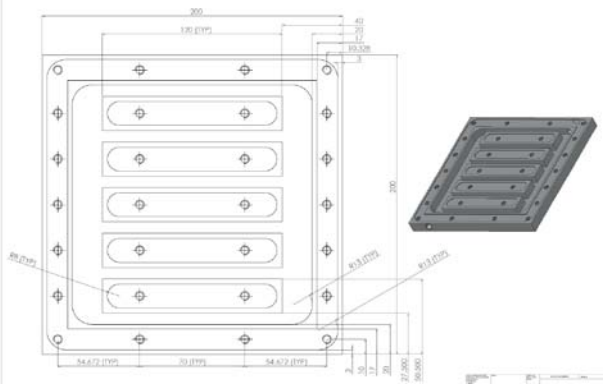

Figure 3 Drawing of Al flux target.

Redox pair selection

The pertinent literature lists several hundreds of thermochemical cycles for the production of hydrogen. They either use concentrated solar energy or heat from nuclear fission. 2-step cycles typically have a maximum temperature of approximately 2200 °C under atmospheric conditions. This poses a series of material and design challenges. Multi-step cycles (3 and more steps) typically have lower maximum temperatures around 1200 °C. However, they are more complex and energetically less efficient. Simple, 2-step cycles will benefit most from reduced process temperatures. Therefore, only 2-step cycles are considered. Abanades et al. [3] have carried out an extensive screening of potentially interesting water-splitting cycles. Furthermore Kodama and Gokon [4], Perkins and Weimer [5], and Steinfeld [6] have published reviews of potentially beneficial water splitting cycles. Table 1 summarizes relevant 2-step cycles.

TABLE 4 2-STEP THERMOCHEMICAL WATER SPLITTING CYCLES.

#	Cycle	Reactions	Process temperature under atmospheric conditions (°C)
1	Zn/ZnO	$ZnO \rightarrow Zn + O_2$	2000 [3]
		$Zn + H_2O \rightarrow ZnO+H_2$	1100 [3]
2	Fe_3O_4/FeO	$Fe_3O_4 \rightarrow 3\ FeO + ½\ O_2$	2200 [3]
		$3\ FeO + H_2O \rightarrow Fe_3O_4 + H_2$	400 [3]
3	In_2O_3/In_2O	$In_2O_3 \rightarrow In_2O+1/2\ O_2$	2200 [3]
		$In_2O+2H_2O \rightarrow In_2O_3+2H_2$	800 [3]
4	SnO_2/Sn	$SnO_2 \rightarrow Sn+O_2$	2650 [3]
		$Sn+2H_2O \rightarrow SnO2+2H_2$	600 [3]
5	MnO/$MnSO_4$	$MnSO_4 \rightarrow MnO+SO_2+1/2O_2$	1100 [3]
		$MnO+H_2O+SO_2 \rightarrow MnSO_4+H_2$	250 [3]
6	FeO/$FeSo_4$	$FeSO_4 \rightarrow FeO+SO_2+1/2O_2$	1100 [3]
		$FeO+H_2O+SO_2 \rightarrow FeSO_4+H_2$	250 [3]
7	CoO/$CoSO_4$	$CoSO_4 \rightarrow CoO+SO_2+1/2O_2$	1100 [3]
		$CoO+H_2O+SO_2 \rightarrow CoSO_4+H_2$	200 [3]
8	Fe_3O_4/$FeCl_2$	$Fe_3O_4+6HCl \rightarrow 3FeCl_2+3H_2O+1/2O_2$	1500 [3]
		$3FeCl_2+4H_2O \rightarrow Fe_3O_4+6HCl+H_2$	700 [3]
9	Mo/Mo_2	$MoO_2 \rightarrow Mo+O_2$	3700 [3]
		$Mo+2H_2O \rightarrow MoO_2+2H_2$	1550 [3]
10	SoO_2/SiO	$SiO_2 \rightarrow SiO + 1/2\ O_2$	3000 [3]
		$SiO+H_2O \rightarrow SiO_2+H_2$	2650 [3]
11	W/WO_3	$WO_3 \rightarrow W+3/2\ O_2$	3900 [3]
		$W+3H_2O \rightarrow WO_3+3H_2$	900 [3]
12	Hg/HgO	$Hg+H_2O \rightarrow HgO+H_2$	360 [3]
		$HgO \rightarrow Hg+1/2O_2$	600 [3]
13	Cd/CdO	$Cd+H_2O \rightarrow CdO+H_2$	25 (electrochemically) [3]
		$CdO \rightarrow Cd+1/2O_2$	1400 [3]
14	CO/CO_2	$CO+H_2O \rightarrow CO_2+H_2$	700 [3]
		$CO_2 \rightarrow CO+1/2O_2$	1700* [3]
15	Ce_2O_3/CeO_2	$CeO_2 \rightarrow Ce_2O_3$	2350 [7]
		$Ce_2O_3+H_2O \rightarrow 2CeO_2+H_2$	500 [3]
16	Mg/MgO	$MgO \rightarrow Mg+1/2O_2$	3700 [8]
		$Mg+H_2O \rightarrow MgO+H_2$	100 [7]
17	SnO/SnO2	$SnO_2 \rightarrow SnO+1/2O_2$	2000 [9]
		$SnO+H_2O \rightarrow SnO_2+H_2$	550 [9]

Selection criteria

Cycles are eliminated based on three criteria:

1. *Toxicity*. Cycles that contain highly toxic substances are eliminated (cycles 12 and 13)
2. *Temperature requirements*. Even though low pressure operation will reduce peak temperatures all cycles with atmospheric peak temperatures above 2500 C are eliminated (cycles 4, 9, 10, 11, 14, 16)
3. *Reaction complexity and side reactions*. Several cycles feature significant side reactions. Chemical equilibrium calculations have been carried out (figures). Cycles 5, 6, 7, and 8 were thus eliminated.

Short list

Based on the above deliberations 5 cycles are selected for further investigation:

1. Fe_3O_4/FeO
2. Ce_2O_3/CeO_2
3. ZnO/Zn
4. SnO/SnO2
5. In_2O_3/In_2O

The Fe_3O_4/FeO is widely regarded as a promising candidate for solar thermochemical fuel productions. Exploratory experiments based on the Ce_2O_3/CeO_2 cycle have shown promise. Reducing the operating pressure promises to be beneficial in both cases. The remaining three cycles ZnO/Zn, SnO/SnO_2, and In_2O_3/In_2O all fall into the category of volatile metal oxide cycles. I.e., the products of the high temperature reduction reaction form a reactive gaseous mixture that must be quenched rapidly to avoid recombination. Thus significant irreversibilities are introduced. Experimental investigations will therefore focus on the iron and cerium based cycles. Volatile metal oxide cycles are nevertheless considered an interesting option and might be reconsidered at a later stage.

Thermodynamic analysis

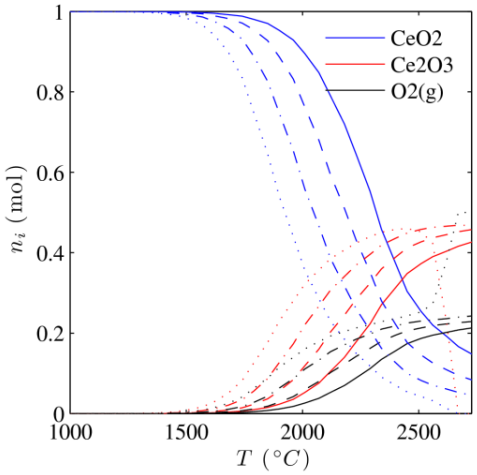

Figure 12 Chemical equilibrium composition for the CeO2/Ce2O3 system as a function of temperature at 1 bar (solid), 0.1 bar (dash), 0.01 bar (dash-dot) and 0.001 bar (dotted)

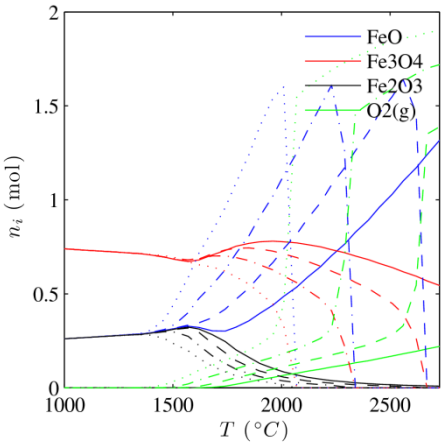

Figure 5 Chemical equilibrium composition for the Fe3O4/FeO system as a function of temperature at 1 bar (solid), 0.1 bar (dash), 0.01 bar (dash-dot) and 0.001 bar (dotted)

Closed system chemical equilibrium calculations for both, the Ce-based system and the Fe-based system have been carried out (Figures 4 and 5). In both cases the pressure dependency is significant. In the Ce-based system, the temperature necessary to obtain 0.25 mole of O_2 per mole of CeO_2 (50% yield) reduces from approximately 2300 °C to 1800 °C. In a solar reactor O_2 will be constantly removed this will further increase the yield. In the Fe system, pressure dependence is even stronger. However, O_2 yield is relatively low. It sharply increases when Fe appears in the gas phase. Thus the Fe-based system may be considered a volatile metal oxide system.

Next steps

Upon completion of simulator construction and characterization, low pressure, high temperature metal oxide reduction experiments will be carried out. A preliminary schematic of the planned experimental setup is shown in figure 5

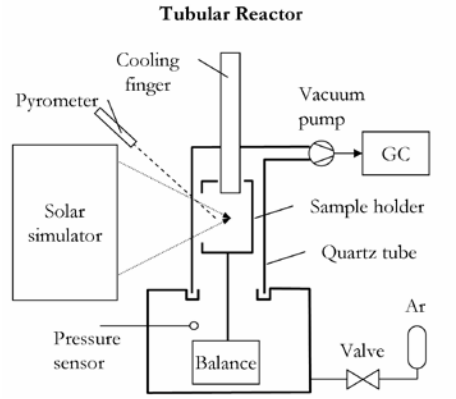

Figure 13 Preliminary schematic of low pressure experimental setup.

Journal Papers

[1] J. Petrasch and P. Coray, "A free and open source Monte Carlo ray tracing program for surface exchange," *Journal of Solar Energy Engineering*. In preparation

Conference Proceedings

[1] J. Petrasch, "A free and open source Monte Carlo ray tracing program for concentrating solar energy research," presented at the ASME 4th International Conference for Energy Sustainability, Phoenix, AZ, 2010.

Presentations

[1] B. Erickson, J. Petrasch"High Flux Solar Simulator for the Investigation of Solar Thermochemical Cycles at Low Pressures", Poster presentation at the Florida Energy Systems Consortium, Summit, Orlando, FL, 2010.

References

[1] J. Petrasch, "A free and open source Monte Carlo ray tracing program for concentrating solar energy research," presented at the ASME 4th International Conference for Energy Sustainability, Phoenix, AZ, 2010.

[2] J. Petrasch and P. Coray, "A free and open source Monte Carlo ray tracing program for surface exchange," *Journal of Solar Energy Engineering*. In preparation

[3] S. Abanades, P. Charvin, G. Flamant, and P. Neveu, "Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy," *Energy*, vol. 31, no. 14, pp. 2805-2822, Nov. 2006.

[4] T. Kodama and N. Gokon, "Thermochemical Cycles for High-Temperature Solar Hydrogen Production," *Chem. Rev.*, vol. 107, pp. 4048-4077, 2007.

[5] C. Perkins and A. W. Weimer, "Likely near-term solar-thermal water splitting technologies," *International Journal of Hydrogen Energy*, vol. 29, no. 15, pp. 1587-1599, Dec. 2004.

[6] A. Steinfeld, P. Kuhn, A. Reller, R. Palumbo, J. Murray, and Y. Tamaura, "Solar-processed metals as clean energy carriers and water-splitters," *International Journal of Hydrogen Energy*, vol. 23, no. 9, pp. 767-774, Sep. 1998.

[7] A. Roine, *HSC Chemistry*. Outotec.

[8] A. Steinfeld and R. Palumbo, "Solar thermochemical process technology," in *Encyclopedia of physical science & technology*, vol. 15, 2001, pp. 237-256.

[9] S. Abanades, P. Charvin, F. Lemont, and G. Flamant, "Novel two-step SnO2/SnO water-splitting cycle for solar thermochemical production of hydrogen," *International Journal of Hydrogen Energy*, vol. 33, no. 21, pp. 6021–6030, 2008.